

while, in the case of the material needed for making a semi-permeable membrane, in addition to taking up the solvent but not the solute, it must be either rigid itself or be capable of being mounted on a rigid support.

These determinations were carried out by my assistant, Mr. Burgess, for whose care and accuracy I wish here to acknowledge my thanks.

Mobility of the Positive and Negative Ions in Gases at High Pressures.

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Introduction and Purpose.

The velocity of ions in gases at reduced pressures was first investigated by Rutherford* and by Langevin.† Recently the author and others have carried out similar investigations. The results of these investigations show that for the negative ions in air the product of the mobility and the pressure is constant for pressures ranging from 760 mm. to 200 mm. of mercury, but with further reduction the product increases with the reduction of pressure, this increase becoming very great at low pressures.‡ For the positive ions in air the product of the mobility and pressure is constant for pressures investigated between 760 mm. and 3 mm. of mercury.§ Similar results were obtained for the mobilities of the ions in other gases. The results show that if the ion is an aggregation of molecules, this aggregation becomes, at low pressures, less complex in the case of the negative ion, while in the case of the positive ion it persists down to 3 mm. of mercury.

The purpose of the present research was the study of the mobilities of both kinds of ions in gases at high pressures. The method of investigation is based on the mathematical expression, developed by Prof. Rutherford,|| for the current between two plates, assuming that a very intense ionisation exists near the surface of one of the electrodes.

* Rutherford, E., 'Camb. Phil. Soc. Proc.,' 1898, vol. 9, p. 401.

† Langevin, N. P., 'Ann. de Chim. et de Phys.,' 1903, vol. 28, p. 289.

‡ Kovarik, Alois F., 'Phys. Rev.,' 1910, vol. 30 (4), p. 415.

§ Todd, G. W., 'Camb. Phil. Soc. Proc.,' 1910, vol. 16, p. 21.

|| Rutherford, E., 'Phil. Mag.,' 1901, vol. 2, p. 210.

The expression developed is

$$i = 9V^2K/32\pi d^3.$$

where i is the current per square centimetre through the gas, K the mobility of the ions, V the potential difference, and d the distance between the plates.

Rutherford* verified this equation experimentally, using for the intense surface ionisation, ionisation produced by a heated platinum plate. C. D. Child,† who developed the same equation independently, utilised it for the measurement of the velocity of ions drawn from flame gases.

In the present work this equation was again tested experimentally, and was utilised for the purpose of measuring the mobility of the ions in gases at high pressures. The intense surface ionisation was obtained by using a preparation of ionium‡ at one of the plates and reducing the range of the α -particles by using the gas at high pressures. Since ionium is separated with thorium, some β - and γ -rays due to thorium were present. With the specimen used this volume ionisation was not found to be of importance. If β -rays are present in abundance, their volume ionisation superposed on the surface ionisation due to α -particles at high pressure is very noticeable, as was found in an experiment where freshly prepared polonium was used, the polonium containing a considerable amount of radium E, which emits β -rays.

Apparatus.

The apparatus used was a cylinder 8 cm. in diameter and 12 cm. deep, made especially for high pressure work, and shown in fig. 1. The upper electrode in most of the experiments was 1.054 cm. in radius, and was encircled by a guard ring. The insulation was amber. The lower electrode was held in position by ebonite fastened at the bottom of the cylinder, and was connected with the battery. The gas passed into the cylinder through a valve at the lower part of the cylinder, and its pressure was measured by an attached calibrated gauge.

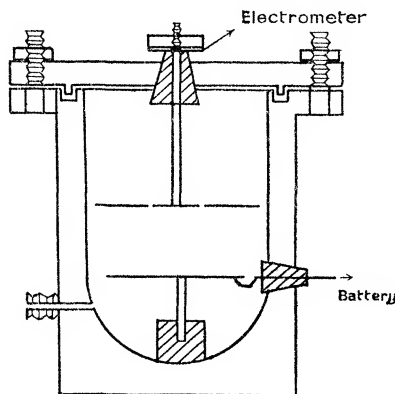


FIG. 1.

The ionium was spread as a very thin layer over a plate 6 cm. in diameter, and this plate served as the lower

* Rutherford, E., 'Phys. Rev.', 1901, vol. 13 (6), p. 321.

† Child, C. D., 'Phys. Rev.', 1901, vol. 12 (3), p. 137.

‡ This material was part of the ionium separated by Prof. Boltwood from the radioactive residues loaned by the Royal Society to Prof. Rutherford ('Roy. Soc. Proc.', 1911, A, vol. 85, p. 77).

electrode. In order to protect the ionium from sudden gusts of gas, a cylinder of ebonite was placed round the wall inside the cylinder. By means of keys the lower plate could be brought to a positive or negative potential. An electrometer with condensers of suitable capacities was used to measure the current between the electrodes.

Test of the Equation.

Experiments were first carried out to test the equation. In order to find out if the equation is applicable to the present problem, it was necessary to show:—

- (1) That the current varies as the square of the potential difference.
- (2) That the current varies inversely as the cube of the distance.
- (3) That the ionisation produced by the α -particles of the ionium used was sufficiently great, so that any increase in the ionisation had no effect on the current for a given potential difference and a given distance.

These experiments were carried out in air. The air was first compressed into a large cylinder to 120 atmospheres by means of a liquid air compressor. The amount of moisture present at this pressure must be small. From this cylinder it was passed very slowly into the apparatus so as not to scatter the active material. When a desired pressure was reached it was necessary to wait some time before taking measurements on account of the motion and the changing temperature of the gas.

The method of taking readings was to measure the time of deflection of the spot of light over a definite calibrated portion of a scale. This was done for both positive and negative currents for every potential. Readings for a given potential difference were taken often in each set and were used as a check.

Table I gives the results of an experiment when the pressure of the air was 59.5 atmospheres, and the distance between the plates was 2.81 cm. The potential difference is given in volts and the current per centimetre in E.S.U. These results are shown graphically in fig. 2. If the currents are plotted against the square of the potential difference, a straight line passing through the origin is obtained for the first 80 volts. Above 80 volts, there is a deviation from the square of the potential difference law. The range of voltage for which the current is proportional to the square of the potential difference varies for different pressures and also for different distances, being greater for higher pressures and greater for greater distances. It is within this range of potential difference, where the law holds, that the current must be determined for the calculation of the mobility of the ions. This was done in all cases by obtaining a set of

readings similar to those of Table I, plotting the currents against the square of the potential difference and then selecting some convenient value for the potential difference and measuring the value of the current on the graph.

Table I.—Air.

Pressure = 59·5 atmospheres. $d = 2.81$ cm. $T = 19^\circ \text{C.}$

P.D., in volts.	Square of P.D.	Current in E.S.U. per cm. ² .	
		Positive.	Negative.
6	36	2.3×10^{-5}	1.48×10^{-5}
10	100	3.8	4.98
14	196	7.0	9.4
20	400	13.0	18.2
26	676	20.6	32.0
32	1024	32.6	46.5
41	1681	49.5	68.6
51	2601	77.2	108
61	3721	112	161
71	5041	142	206
82	6724	187	263
123		356	410
164		509	564
205		630	646
287		748	807
492		966	1040

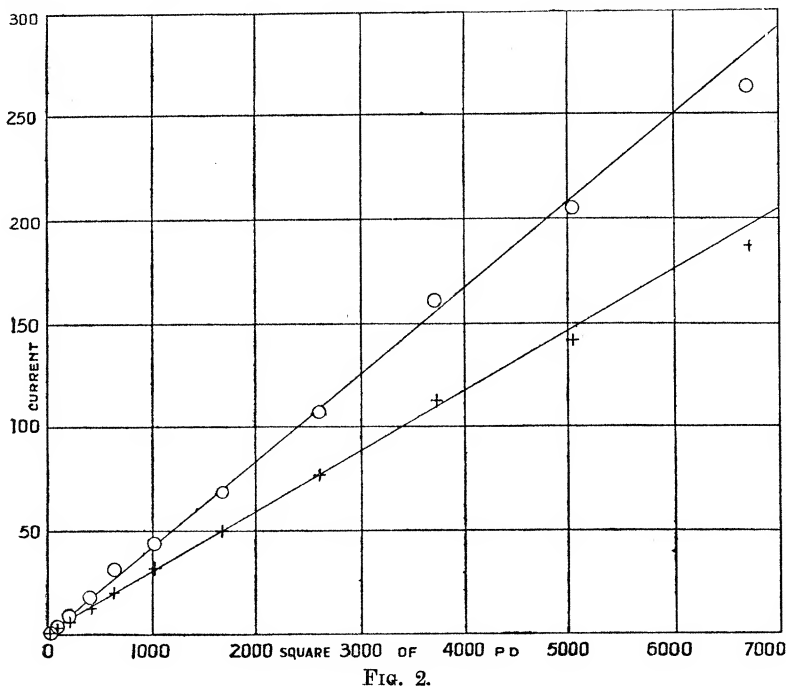


FIG. 2.

In testing the equation for distance, measurements were made for current for a potential difference of 30 volts for different distances. The pressures were all above 30 atmospheres, and the current, which, as will be seen, varies inversely with the pressure (in air), was reduced to the value for the mean pressure of all the experiments, viz., 50 atmospheres. The product of the current per square centimetre thus obtained and the cube of the distance between the plates is given in Table II for the various distances used.

Table II.—Various Distances between Electrodes.

Air at 50 atmospheres. P.D. = 30 volts = 0.1 E.S.U. T = 19° C.

Distance, in cm.	d^3 .	$i \times d^3$. i in E.S.U. per cm. ² ; d in cm.	
		Positive.	Negative.
0.805	0.52	8.3×10^{-3}	10.4×10^{-3}
1.36	2.52	7.4	9.7
1.53	3.58	7.6	10.2
1.76	5.45	7.7	10.3
2.31	12.33	7.6	10.1
2.81	22.2	7.3	10.2
3.27	35.0	7.0	9.3
3.78	54.0	7.2	9.4
4.27	77.8	6.8	8.9

It will be noticed that the values of this product are reasonably constant although the cube of the distance changed in the ratio of 1 to 150. With the greater distances, the values are somewhat lower, due, no doubt, to the fact that the field became less uniform. On the whole, however, the results may be considered fairly satisfactory in proving that, for the distances used, the current varies inversely as the cube of the distance between the plates.

After a series of experiments the amount of ionium was considerably increased, the layer still being extremely thin. The current for a definite potential difference and distance between the plates, and for a definite pressure, did not change, which shows that the surface ionisation was intense enough, and that the current was independent of further increase in the intensity of the ionisation.

Experiments with Air.

In the experiments to determine the mobility of the ions at various pressures, care had to be taken in the choice of the distance between the plates for the following reasons: At lower pressures the range of the α -particle becomes greater and the correction for this range becomes appreciable for small distances. The correction for the range of the

α -particles consisted in decreasing the distance between the electrodes by one half of the range at the particular pressure used. With great distances between the plates the field could not be made uniform on account of the small dimensions of the apparatus. With distances between 2 and 3 cm., however, the field appeared to be quite uniform and the correction for the range was small for the high pressures.

The results obtained for the various pressures in air are given in Table III. The actual mobilities in centimetres per second per volt per centimetre for the two kinds of ions, as deduced from Rutherford's equation, are given, and also the products of the mobility and the pressure in atmospheres. It will be noticed from the results that the velocity varies inversely with the pressure up to 75 atmospheres. The mean values for the product of the mobility and pressure in atmospheres for pressures above 30 atmospheres at a temperature of 19° C. are 1·89 and 1·346 for the negative and the positive ions respectively, with a ratio of 1·405. The values obtained by Zeleny* at atmospheric pressure, and at a temperature of 13·5° C., are respectively 1·87 and 1·36, giving a ratio of 1·375.

Table III.—Air. Mobility at various Pressures.

$d = 2\cdot81$ cm. $T = 19^\circ$ C.

Pressure, in atmospheres.	Mobility, in cm./sec. per volt/cm.		Mobility $\times$ Pressure.		Ratio of mobilities.
	Positive.	Negative.	Positive.	Negative.	
74·6	0·0187	0·0262	1·39	1·96	1·41
70·6	0·0192	0·0270	1·36	1·91	1·40
59·5	0·0226	0·0318	1·34	1·89	1·41
53·0	0·0258	0·0366	1·37	1·94	1·41
50·6	0·0261	0·0366	1·32	1·85	1·40
47·6	0·0272	0·0392	1·30	1·86	1·43
41·7	0·0317	0·0449	1·32	1·87	1·42
36·8	0·0373	0·0506	1·37	1·87	1·37
31·2	0·0433	0·0600	1·35	1·87	1·39
21·1	0·0615	0·0830	1·30	1·75	1·35
13·3	0·103	0·138	1·37	1·84	1·40
Mean.....			1·346	1·89	1·405

Experiments with Carbon Dioxide.

In these experiments a cylinder of carbon dioxide was used. The gas was found to be saturated with moisture, and to contain about 0·3 per cent. of air, a trace of HCl, and a slight trace of alcohol. On letting the gas into the

* Zeleny, J., 'Phil. Trans.,' 1900, A, vol. 195, p. 193.

apparatus, the insulation generally broke down. Attempts were made to dry the gas partially by placing calcium chloride into the apparatus and letting the apparatus stand for a day. The insulation never broke down in this case, and the negative ions were found to have a greater velocity than the positive ions, but consistent results could not be obtained for some reason. As arrangements were not made to dry the gas previous to passing it into the apparatus, the only results included are those for the moist gas. These results are given in Table IV. It will be noticed that the product of the mobility and the pressure is practically constant up to a pressure of 40 atmospheres, but that it decreases considerably as the gas approaches the liquid state. The mobility of the positive ions in moist carbon dioxide is greater than the mobility of the negative ions, as was also observed by Zeleny and others, the ratio of mobilities being 0.95 for pressures up to 40 atmospheres and unity for pressures above 50 atmospheres. The mean values of the product of the mobility and pressure in atmospheres taken for pressures up to 40 atmospheres and 19° C. are 0.705 and 0.67 for the positive and negative ions respectively. Zeleny's values at atmospheric pressure and 17° C. are 0.82 and 0.75 respectively, giving a ratio of 0.92.

Table IV.—Carbon Dioxide (moist). Mobility at various Pressures.

$$d = 2.31 \text{ cm. } T = 19^\circ \text{ C.}$$

Pressure, in atmospheres.	Mobility in cm./sec. per volt/cm.		Mobility $\times$ Pressure.		Ratio of mobilities.
	Positive.	Negative.	Positive.	Negative.	
57.0	0.0091	0.0091	0.52	0.52	1.00
52.4	0.0116	0.0116	0.61	0.61	1.00
46.7	0.0137	0.0136	0.64	0.63	0.98
41.8	0.0160	0.0148	0.67	0.62	0.93
36.7	0.0187	0.0181	0.69	0.66	0.96
31.5	0.0234	0.0225	0.74	0.71	0.96
26.0	0.0264	0.0254	0.69	0.66	0.96
21.1	0.0355	0.0340	0.75	0.72	0.95
15.3	0.0465	0.0427	0.71	0.65	0.92
10.2	0.0732	0.0679	0.75	0.69	0.93
Mean for values for pressure up to 40 atmos. ...			0.705	0.67	0.94

Experiments with Hydrogen.

The hydrogen used in these experiments contained 0.7 per cent. nitrogen and very little moisture (about 0.02 per cent.). The range of the α -particles in hydrogen is four times that in air, consequently greater pressures were necessary to realise the condition of surface ionisation. The results of the

experiments are given in Table V. It will be noticed that the mobility varies inversely as the pressure up to 72·5 atmospheres—the highest pressure used in the experiments. The mean values of the product of the mobility and pressure in atmospheres at 20° C. are 8·19 and 6·20 for the negative and the positive ions respectively, giving a ratio of mobilities equal to 1·32. The mobilities for the negative and positive ions in hydrogen at atmospheric pressure and 20° C., as found by Zeleny, are 7·95 and 6·70 respectively, giving a ratio of mobilities equal to 1·19.

Table V.—Hydrogen. Mobility at various Pressures.

$$d = 2.31 \text{ cm. } T = 20^\circ \text{ C.}$$

Pressure, in atmospheres.	Mobility, in cm./sec. per volt/cm.		Mobility $\times$ Pressure.		Ratio of mobilities.
	Positive.	Negative.	Positive.	Negative.	
72·5	0·084	0·110	6·10	8·00	1·31
68·4	0·090	0·120	6·15	8·25	1·34
62·7	0·096	0·126	6·01	7·90	1·31
58·1	0·105	0·139	6·10	8·08	1·32
52·8	0·116	0·153	6·14	8·10	1·32
47·3	0·132	0·175	6·25	8·29	1·32
41·9	0·146	0·198	6·11	8·30	1·36
36·7	0·170	0·228	6·25	8·38	1·34
31·5	0·201	0·267	6·34	8·41	1·33
25·7	0·248	0·322	6·38	8·28	1·30
20·8	0·305	0·388	6·35	8·08	1·27
Mean.....			6·20	8·19	1·32

Summary.

The mobilities of the positive and negative ions in dry air, dry hydrogen, and moist carbon dioxide were measured. The method of measurements is based on Rutherford's equation for the velocity of ions between two plates, the assumption in the theory being that a strong surface ionisation exists at one of the plates. This assumption was satisfied experimentally by using the α -particles from ionium as the ionising agent, and reducing their range by using the gases at high pressure. The equation was tested experimentally.

The results for the mobilities of the ions in these gases are as follows: In dry air and dry hydrogen the mobility varies inversely as the pressure up to 75 atmospheres, the highest pressure used. In moist carbon dioxide the product of the mobility and pressure is constant for pressures up to

40 atmospheres, but for higher pressures the product decreases as the gas approaches the liquid state.

The mean values for the products of the mobility and pressure in atmospheres, for the range of pressures for which the product was constant, are, for the negative and positive ions respectively, in dry air, 1.89 and 1.346; in dry hydrogen 8.19 and 6.20, and moist carbon dioxide 0.67 and 0.705 cm. per second for a potential gradient of 1 volt per centimetre.

In conclusion, I take great pleasure in expressing my best thanks to Prof. Rutherford for suggesting this research, and for the valuable advice given by him during the progress of the experiments.

On the Viscosities of Gaseous Chlorine and Bromine.

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Introduction.

The object of the experiments about to be described was to determine the viscosities, at various temperatures, of gaseous chlorine, bromine, and iodine, by comparison with air. The apparatus, however, proved unsuitable in several respects for working at the higher temperatures required. It has, nevertheless, yielded satisfactory results at the lower temperatures; and the viscosity of chlorine at atmospheric temperature and at 100° C., and that of bromine at the latter temperature only, have been measured by means of it. These values are now published, pending the extension of the investigation on the lines indicated, with a new form of apparatus which promises to be entirely adequate for the purpose.

The chief difficulty which presents itself in working with the halogen gases is the readiness with which they attack mercury. On this account, the method I have previously used* for viscosity determinations was rendered unsuitable; but it has been found possible to retain one of its most desirable features, viz., the mercury pellet, which serves the double purpose of creating a constant pressure difference, and of measuring the volume of

* 'Roy. Soc. Proc.,' A, vol. 83, pp. 265 and 516.